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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

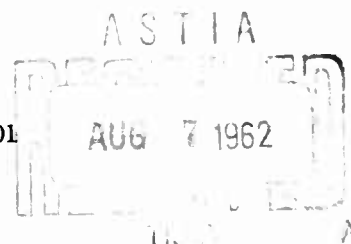## ON THE EXISTENCE OF GASEOUS SULPHIDES OF THE TRANSITION ELEMENTS

TECHNICAL DOCUMENTARY REPORT No. WADD-TR-60-782, PART IV

MAY 1962

DIRECTORATE OF MATERIALS AND PROCESSES
(MATERIALS CENTRAL)
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

ASTIA

AUG 7 1962

YEARS
OF
MATERIALS
PROGRESS

SAPPHIRE ANNIVERSARY

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FOREWORD

This report was prepared by the University of Brussels, Brussels, Belgium under USAF Contract No. AF 61(052)-225. The Contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials", Task No. 735001, "Non-Graphitic". The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer. This report covers work done from April 1961 to April 1962.

WADD Technical Report 60-782, Parts I, II, III, V, VI have already been published, Parts VII and VIII are in preparation.

ABSTRACT

Thermodynamic considerations permit us to predict the mode of vaporization of transition element sulphides. MnS is the only clear case where the gaseous sulphide molecule has an appreciable concentration in the saturated vapor. This is confirmed by a mass spectrometric investigation which gave us the measurement D_0^o (MnS) = 65 $\pm$ 5 Kcal/mole.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.
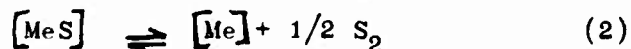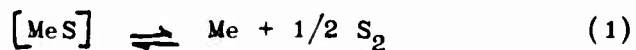
FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

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ON THE EXISTENCE OF GASEOUS SULPHIDES OF THE TRANSITION ELEMENTS

The Dissociation Energy of Gaseous MnS

It is very important to obtain information on the lattice energy, $\Delta H^o_o[\text{at}]$, of solids, and dissociation energies, D^o_o, of gaseous molecules of whole groups of compounds such as homonuclear molecules[1], oxides[2], sulphides[3] etc. and to study the variation of these properties, or ratio of these magnitudes, $\Delta H^o_o[\text{at}]/D^o_o = \alpha$, as a function of the electronic structure of the constituting atoms. An interesting case is that of the sulphides of transition elements.

The simplest discussion of the mechanism of vaporization of solid sulphides $[\text{MeS}]$ can be based on three processes:

$$[\text{MeS}] \rightleftharpoons \text{Me} + 1/2\ S_2 \qquad (1)$$

$$[\text{MeS}] \rightleftharpoons [\text{Me}] + 1/2\ S_2 \qquad (2)$$

$$[\text{MeS}] \rightleftharpoons \text{MeS} \qquad (3)$$

(condensed phases, solid and liquids, are marked by square brackets $[\ ]$, gases without brackets). Complications that occur when instead of reaction (2) stoichiometric compounds

such as $[Me_2S]$ or non stoichiometric solids $[Me_xS_y]$ are formed are not discussed here in detail. Association of S_2 is not discussed, dissociation shall be mentioned.

Which of the processes (1) or (2) predominates is seen immediately by considering the equilibrium

$$S_2 + 3[Me] \rightleftharpoons 2[MeS] + Me \qquad (4)$$
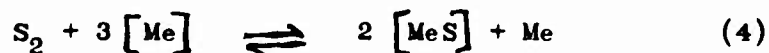
and the magnitude

$$A = 3\Delta H_o^o[vapMe] + D_o^o(S_2) - 4\Delta H_o^o[atMeS] + T\Delta fef\left\{2[MeS] + Me - S_2 - 3[Me]\right\} \quad (5)$$

where $\Delta H_o^o[vapMe]$ is the heat of vaporization of one atom-gram $[Me]$, $\Delta H_o^o[atMeS]$ the heat necessary to transform one half molecule-gram $[MeS]$ in the constituting gaseous atoms, $D_o^o(S_2) =$ 100 kcal[3] the dissociation energy of S_2 and Δ fef the difference in free energy functions of the substances given in the braces $\{\}$.

If $A > 0$ process (2) predominates and

$$- RT\ln p(Me)/p(S_2) = A = \Delta H_o^o + T\Delta fef \qquad (6)$$

For the first row of transition elements sulphides[4,5] $\Delta fef \approx - 5$ e.u. ; the dominant term is the enthalpy difference which from FeS to CuS lies in the narrow limits $\Delta H_o^o(6) \approx + 24 \pm 3$ kcal (well within error limits) i.e. $p(Me)/p(S_2) \approx 10^{-4}$ at 1000°K and 10^{-2} at 2000°K. In this case the relation

$$-RT\ln p(S_2)/p(MeS) = D_o^o(MeS) + 2\Delta H_o^o[atMeS] - D_o^o(S_2) - 2\Delta H_o^o[vapA]$$
$$+ T\Delta fef\left\{2[Me] + S_2 - MeS - [MeS]\right\} \quad (7)$$

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is obtained from the equilibrium

$$MeS + \left[MeS\right] \rightleftharpoons S_2 + 2\left[Me\right] \qquad (8)$$
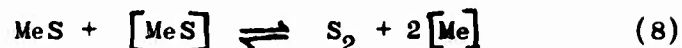
Δfef is again small, about $+ 3$ e.u.; from a comparison of oxides and sulphides one obtains $D_o^o(MeS) \approx 60$ to 70 kcal and $\Delta H_o^o(7) \approx - 40$ to -50 kcal for FeS, CoS, CuS. Thus $p(MeS)/p(S_2)$ increases with increasing temperature but even at $2000^{\circ}K$ reaches only 10^{-3} to 10^{-4}. This is not easily reconciled with Hsiao and Schlechten's[6] results indicating 20 to 54% Fe and Co transfer in the vaporization of FeS and CoS ; these results would mean that $D_o^o(MeS) \approx 100$ kcal. An explanation might be in the terms of more complicated gaseous sulphides such as Fe_2S, Fe_2S_3 or gaseous polymers. Finally $-RT\ln p(S)/p(S_2) \approx D_o^o(S_2) + \Delta H_o^o\left[vapMe\right] - 2\Delta H_o^o$ at $\left[MeS\right]$ leads to $p(S_2) \approx 10$ to 100 $p(S)$. If $\left[Me\right]$ reacts with $\left[MeS\right]$ to give stoichiometric or non stoichiometric compounds $p(S_2)/p(Me)$ is even larger.

In the first row of transition elements MnS is the only clear case of $A < 0$ (eq.5), with $\Delta H_o^o = - 64$; at the end of this row for ZnS and GaS $\Delta H_o^o = - 99$ and $- 59$ kcal respectively. For the oxides ΔH_o^o is strongly negative with the exception of CuO $(+ 6$ kcal$)$, where however probably the actual process is $\left[CuO\right] \rightleftharpoons 1/2 \left[Cu_2O\right] + 1/2\ O_2$. For negative ΔH_o^o, i.e. process (1)

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the ratio $p(S_2)/p(MeS)$ is obtained from the equilibrium:

$$MeS \rightleftharpoons 1/3[MeS] + 1/3 \, S_2 + 2/3 \, Me \qquad (9)$$

and
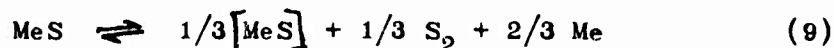
$$-RT\ln p(S_2)/p(MeS) = D_o^o(MeS) - 2/3\Delta H_o^o [atMeS] - 1/3 D_o^o(S_2) + 2/3RT\ln 2$$
$$+ T\Delta \, fef\left\{1/3[MeS] + 1/3 \, S_2 + 2/3 \, Me - MeS\right\} \qquad (10)$$

For MeS an estimate similar to that above, gives

$-\log p(S_2)/p(MeS) \approx -6500/T + 1.5$ using the mass spectrometric

vaporization technique described previously[7] experiments

were carried out with MnS between 1800° and 1900°K: at 1850°K

$\log p(S_2)/\log p(MnS) = 2.1$ From eq.(10) $D_o^o(MnS) = 65 \pm 5$ kcal

was obtained. For this third law method free energy functions

of MnS were calculated from $r_e = 2.1$ A and $\omega_e = 540$ cm^{-1}, the

data from[5] were taken for Mn and S_2. Further $\Delta H_{298}^o f[MnS] =$

49.0 ± 0.5 kcal[8,9,4]: $S_{298}^o[MnS] = 18.7 \pm 0.3$ e.u.[10] and

$C_p[MnS] = 11.4 + 1.8 \times 10^{-3}T$ [11] yield $\log p(Mn) = -3.00 \pm 0.35$;

pressure calibrations by complete vaporization of weighed

samples yield $- 3.44$. Also $-RT\ln p(S)/p(S_2) \approx 2/3\left\{D(S_2) - \Delta H_o^o [atMnS]\right\}$

is in agreement with experiment.

For VS, TiS, CrS there are no data, however $\Delta H_o^o [atMeO] -$

$\Delta H_o^o [atMeS] = 16.5 \pm 2$ kcal for Ca, Mn, Co, Ni ; assuming this

difference to be constant ΔH_o^o of eq.(6) is for these three

sulphides -70 ± 10 kcal. Assuming $D_o^o(MeO) - D_o^o(MeS) \approx 30$ kcal

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as for oxides and sulphides of group II^A, IV^B and Mn one finds: $-\log p(S_2)/p(MeS) \approx -3300/T + 1.5$ and $P(S) \approx 10 p(S_2)$: a favorable situation for observing gaseous sulphides.

For the two other rows of transition elements it seems difficult to make predictions, for the rare earths however one would expect to find gaseous sulphides since $\Delta H_o^o[vapMe]$ is relatively low and $D_o^o(MeO)$ high[12].

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